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APPLICATION FOR U.S. LETTERS PATENT

for a new and useful invention entitled:

CURABLE ELASTOMERIC ADHESIVE COMPOSTIONS

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CURABLE ELASTOMERIC ADHESIVE COMPOSITIONS

FIELD OF THE INVENTION

[0001] The present invention relates to adhesive compositions for use in the building and construction industry.

BACKGROUND OF THE INVENTION

[0002] Butyl rubber-based adhesive compositions are known in the building and construction industry. Such adhesive compositions are often formulated with non-crosslinked copolymers of polyisobutylene and isoprene that exhibit cold flow characteristics under certain conditions, for example, under a constant load or gravitational influences over a long duration. Further, upon exposure to extremes of light or temperature, such conditions may lead to chain scission, loss of elasticity, or other characteristics that make the use of adhesive compositions based on non-crosslinked butyl rubbers unsuitable or uneconomical for many applications. In some instances, although addition of some pre-crosslinked butyl rubber components may be used to overcome these undesirable characteristics, dispersion of those components during manufacture, as well as the cost of such materials, remain as obstacles to their widespread or economical use in many applications.

[0003] These considerations are particularly important in certain markets in the building and construction industry. As one example only, and without limitation, there remains a need for suitable and economical adhesives for use in remodeling projects, such as the re-fitting of bathroom fixtures, tubs, and walls with replacement bath linings, including among them, acrylic bathliners and shower walls.

[0004] The present invention addresses this need by providing, among its embodiments, a curable elastomeric adhesive composition which provides increased strength while allowing a reduction in rubber content and corresponding production cost.

SUMMARY OF THE INVENTION

[0005] The present invention comprises an adhesive composition based on the chemical curing of halogenated isobutylene/para-methylstyrene copolymer. Amine-containing compounds are used as curatives to provide controlled curing. The backbone of the halogenated para-methylstyrene-isobutylene copolymer of the invention contains no unsaturation. Accordingly, among its embodiments, without limitation, the present invention provides a cured elastomeric adhesive composition with increased ultraviolet light and heat resistance, along with good high temperature performance and good durability.

[0006] In some embodiments, the invention is an adhesive composition comprised of a halogenated copolymer of isobutylene and paramethylstyrene, tackifier, one or more fillers, and an amine curative agent. Optionally, the embodiment also comprises an antioxidant. In other embodiments, the invention is an adhesive tape comprised of a layer of a cured adhesive composition in the form of a strip on a release liner, said adhesive composition comprised of a halogenated copolymer of isobutylene and paramethylstyrene, tackifier, one or more fillers, and an amine curative agent, and optionally, an antioxidant.

[0007] Other aspects and embodiments of the invention will be apparent to those skilled in the art after reviewing the detailed description below.

DETAILED DESCRIPTION

[0008] The present invention is comprised of a curable elastomeric adhesive composition that includes a halogenated copolymer of isobutylene and paramethylstyrene, tackifier, one or more fillers, and an amine curative agent, and optionally, an antioxidant. In some embodiments, the cured adhesive composition comprising the present invention is in the form of a strip on a release liner.

[0009] The present invention may be comprised of any halogenated copolymer component that provides rubber content suitable for crosslinking under appropriate conditions. Acceptable halogenated copolymers include, without limitation, brominated copolymers of isobutylene and paramethylstyrene available under the trade names Exxpro 3035, Exxpro 3433, and Exxpro 3745 (Exxon Chemical), with Exxpro 3433 being most preferred.

[0010] The cured adhesive composition also includes at least one tackifier or plasticizer. Suitable tackifiers or plasticizers will be known to those of ordinary skill in the art and are available commercially, for example, as Indopol H100 or Indopol H1500 (BP Amoco Chemical Co.), Piccopale 100 (Hercules Inc.), or Escorez 2101 (ExxonMobil Chemical).

[0011] The invention is also comprised of one or more fillers. Such fillers may comprise, without limitation, common fillers, as some examples only, calcium carbonate (for example, Quincy 325 available from Quincy Carbonates), barium sulfate, and clay, and reinforcing fillers, such as talc (for example, Magsil 399 from Whittaker Clark Daniels), precipitated silica (for example, Ultrasil VN3SP available for Degussa Corporation), and carbon black.

[0012] An amine-containing curative agent is used to promote cross-linking of the halogenated copolymer component and thereby enhance desired strength and performance characteristics. Acceptable amine curative agents include, without limitation, triethylenetetraamine (e.g., "TETA", from Dow Chemical Company), hexamethyleneamine (e.g., "HEXA," from Wright Chemicals), 2-methylpentamethylenediamine (e.g., "Dytek A" from Dupont), and 1, 3-pentanediamine (e.g., "Dytek EP" from Dupont). The content of the curative agent and/or the halogenated copolymer component may be varied to adjust the desired cure rate of the adhesive composition.

[0013] The invention may also comprise an antioxidant as a processing stabilizer. Suitable antioxidants include, without limitation, Wingstay L available from Goodyear Chemical. In some embodiments, without limitation, other processing aids known to those of ordinary skill, such as paraffinic oil, may be used.

[0014] For end uses in environments with an increased possibility of microbial growth, the invention may comprise a suitable antimicrobial additive or biocide known to those of ordinary skill, as one example only, diiodomethyl-p-tolysulfone, available under the trade name Amical 48.

[0015] Without limitation, Table 1 describes, in weight percent, formulations of certain embodiments in accordance with the invention:

TABLE 1

Sub-Component	Suitable	Preferred
Exxpro 3433	1-15%	4-8%
Antioxidant	0.01-1%	0.05-0.5%
Biocide	0.01-1%	0.01-0.2%
Tackifiers/plasticizers	10-30%	15-25%
Fillers	50-90%	60-80%
Reinforcing Fillers	0.5-10%	1-5%
Amine Curing Agent	0.001-1%	0.01-0.1%

[0016] The following is exemplary of the general process for producing embodiments of the claimed invention. Times and temperatures can vary depending on the batch size and the mixer used.

[0017] Mixing is done in a sigma blade mixer. First the halogenated copolymer component is masticated in the oil-heated mixer for about five minutes. Next, precipitated silica (Ultrasil VN3SP), antioxidant (Wingstay L), one-third of the filler component (calcium carbonate) and one-third of the tackifier component (polybutene) are added and mixed for about thirty-five minutes or until the mixture is generally homogeneous in appearance and without substantial rubber lumps. The remaining filler and tackifier components are added in two steps and mixed for five minutes in each step. When the mixture is a smooth paste, the curative is added, and the mixture is monitored for changes in consistency. The mixture is then placed in tubs for extrusion.

[0018] A rubber extruder is used, and extrusion takes place according to methods known to those of ordinary skill. Barrel and die temperature are kept at around 180°F. A positive feed of the extruder should be maintained to prevent air entrapment. The extrudate should be cooled as quickly as possible for good roll winding. The mastic obtained from the mixing process is then extruded into tapes of optional dimensions according to the targeted end use. Release paper used in accordance with the invention may comprise siliconized papers comprising with various dimensions.

Examples

[0019] Exemplary compositions comprising the invention were prepared and tested for physical properties as indicated in Table 2, 3 and 4 below. Peel strength measurements were conducted on an Imass SP-2000 peel tester. Samples of 2-mm thickness with masking tape backing were tested. Samples were pressed on a 4.5 pounds roller and dwelled for 1 hour before testing. A peel speed of 12 inches/minute was used. Cone penetration was measured on a Kohler penetrometer per ASTM D217 with following modification. Tape samples of the dimension 2" x 1" x 1" were conditioned in a 77° F water bath for 1 hour before testing. Tensile adhesive strength was measured per ASTM C907 using aluminum discs on a MTS tensile machine. AAMA sag tests were conducted at 180° F for 14 days in an air-circulating oven per AAMA 804.3-92 specifications.

TABLE 2

Examples	1	2	3	4
% by weight				
Sub-components				
Exxpro 3433	4.60	6.50	5.01	6.50
Antioxidant	0.13	0.13	0.13	0.13
Piccopal 100	2.15	2.15	--	--
Escorez 2394	--	--	--	3.00
Amical 48	--	--	0.04	--
Polybutene	13.05	12.38	21.18	13.20
Oil	6.14	5.90	--	4.50
Calcium carbonate	68.31	67.34	71.53	67.56
Talc	3.84	3.84	0.00	3.65
Precipitated silica	1.69	1.69	2.07	1.40
Amine curative	0.09	0.07	0.04	0.07
Specific Gravity (ASTM D792)	1.79	1.77	1.73	1.76
Initial cone penetration (ASTM D217)	105	87	105	75
90° Peel Strength @77°F, pli (ASTM D903-98 modified)	6.1 CF*	6.1 CF	6.7 CF	6.8 CF
Tensile Strength @77°F, psi (ASTM C907)	20 CF	20 CF	25 CF	30 CF
Sag (AAMA 807.3-92)	Pass	Pass	Pass	Pass
Vehicle Bleedout (ASTM C772)	Pass	Pass	Pass	Pass
Resistance to fungus/mildew grow	Excellent	Excellent	Excellent	Excellent
Flexibility (ASTM C765)	Good	Good	Good	Good

*CF = Cohesive failure

TABLE 3

Examples	5	6	7	8	9
% by weight					
Sub-components					
Exxpro 3433	5.00	5.00	5.00	5.00	5.00
Antioxidant	0.13	0.13	0.13	0.13	0.13
Biocide	0.04	0.04	0.03	0.03	0.03
Polybutene	21.15	21.19	20.72	20.72	20.72
Calcium carbonate	67.12	71.56	69.10	69.10	74.10
Talc	3.50	--	5.00	5.00	--
Precipitated silica	3.05	2.07	--	--	--
Amine curative	0.01	0.01	0.01	0.02	0.03
Specific gravity	1.74	1.76	1.76	1.76	1.77
Initial cone penetration (ASTM D217)	103	103	94	93	110
90°Peel strength @77°F, pli (ASTM D903-98 modified)	6.8 *CF	6.6 CF	6.6 CF	9.3 CF	>6 CF
Tensile adhesive strength @77°F, psi (ASTM C907)	23 CF	20 CF	>20 CF	>20 CF	>20 CF
Sag (AAMA 807.3-92)	Pass	Pass	Pass	Pass	Fail
Vehicle Bleedout (ASTM C772)	Pass	Pass	Pass	Pass	--
Resistance to fungus/mildew growth	Excellent	Excellent	Excellent	Excellent	Excellent
Flexibility (ASTM C765)	Good	Good	Good	Good	Good

* CF=Cohesive Failure

[0020] In Table 3, example 5-8 illustrates that talc, used alone or in combination with precipitated silica, improves the sag resistance. In example 9, the formulated material fails on sag resistance when reinforcement fillers are absent.

TABLE 4

Examples	10	11	12
% by weight			
Sub-components			
Kalar 5280	4.60	--	--
XL 10000	--	4.60	--
Exxpro 3433	--	--	4.60
Antioxidant	0.13	0.13	0.13
Biocide	0.03	0.03	0.03
Piccopale 100	1.40	1.40	1.40
Butex	0.05	0.05	0.05
Polybutene	21.00	21.00	21.00
Calcium carbonate	70.69	70.69	70.55
Precipitated silica	2.10	2.10	2.10
Amine curative	--	--	0.13
Specific gravity	1.74	1.74	1.74
Initial cone penetration (ASTM D217)	172	149	129
90°Peel strength @77°F, pli (ASTM D903-98 modified)	<4 *CF	<4 CF	>6 CF
Tensile adhesive strength @77°F, psi (ASTM C907)	<15 CF	<15 CF	>20 CF
Sag (AAMA 807.3-92)	Fail	Fail	Pass
Vehicle Bleedout (ASTM C772)	--	--	--
Resistance to fungus/mildew growth	--	--	Excellent
Flexibility (ASTM C765)	Good	Good	Good

* CF = Cohesive Failure

[0021] In Table 4, these examples show that compounds formulated with commercially available pre-crosslinked butyl rubbers such as Kalar (Elementis Performance Polymers) and XL-10000 (Bayer Corporation) exhibit inferior properties in sag resistance, peel strength, and tensile adhesive strength in comparison to compound formulated with Exxpro rubber crosslinked with amine curative.

[0022] Based on test results presented in Table 2, 3 and 4, embodiments of the invention may comprise those with characteristics falling within specification ranges set out in Table 5.

TABLE 5

Properties	Test Method	Range/Result
Specific gravity	ASTM D792	1.60 - 1.80
Weight per gallon	ASTM D1475	13.0 - 15.0 lbs./gal
Cone Penetration	ASTM D217, 300 grams total weight, 1/10 mm at 77°F	70 – 110
90° Peel Strength	ASTM D903-98 Modified	6-10 pounds per linear inch (pli) with masking tape backing, substrate: acrylic liner; tape thickness: 2 mm
Adhesive Tensile Strength	ASTM C907, metal to metal at 77°F	20-30 pound per square inch (psi). Mode of failure: cohesive
Sag	AAMA 807.3-92	Pass
Vehicle Bleedout	ASTM C772	No exudation of vehicle on Whatman No. 40 filter paper after exposure to 158°F (70°C) for 21 days
Resistance to fungus/ Mildew growth	At 77°F	Excellent
Flexibility	ASTM C765	No cracking or loss of adhesion at -40°F (-15°C) when bent around 3/8 inch mandrel

[0023] While the present invention has been particularly shown and described with reference to the foregoing preferred and alternative embodiments, it is to be understood that this is by way of illustration and not of limitation, and various alternatives to the embodiments of the invention described herein may be employed in practicing the invention without departing from the spirit and scope of the invention as defined in the following claims, which should be construed as broadly as the prior art will permit.